

## PROCESS FOR PRODUCING PHENOL

## BACKGROUND

[0001] The present disclosure generally relates to a method for producing a phenol stream with reduced by-products.

[0002] A three-step cumene process generally produces about 95 percent of the phenol used in the world. Starting from benzene, the three-step cumene process involves (1) alkylation of benzene with propene to form cumene, which is typically catalyzed by phosphoric acid or zeolites; (2) oxidation of cumene to cumene hydroperoxide (also referred to as "CHP") using molecular oxygen; and (3) cleavage of CHP to phenol and acetone, which is typically catalyzed by sulfuric acid.

[0003] The cleavage reaction of CHP in the manufacture of phenol and acetone from cumene is well known. The acid catalyzed cleavage reaction decomposes CHP to form, as primary products, equimolar amounts of phenol and acetone. The CHP decomposition reaction is known to be extremely fast and because of its heavily exothermic nature is typically carried out over a short time period and essentially to completion in most processes. In fact, it is common to use a constant boiling or refluxing type system for the isothermal cleavage reaction. This is generally the constant boiling temperature of the CHP feed stream and product mixture present in the cleavage reactor at a given moment. Generally, this can vary from about 70°C to 90°C. Since this is the general CHP feed stream as well as the reactant product, the phenol to acetone molar ratio is essentially 1 to 1 throughout the course of the reaction.

[0004] In addition to the phenol and acetone products produced by decomposition of CHP because of the acid catalyzed cleavage, unreacted cumene and various other by-products, including alpha-methylstyrene, acetophenone, cumylphenol, dimethylbenzyl alcohol, methylbenzofuran and traces of various "carbonyl-type" impurities including hydroxyacetone (hereinafter also referred to herein as "acetol" and "HA"), mesityl oxide, and aldehydes are usually formed. As a result of these impurities, the resulting phenol and acetone products have to be

separated from these undesirable by-products and impurities. For example, the presence of acetol impurities in the phenol product renders quality unacceptable for many end-use applications, such as in the production of bisphenol-A, diphenyl carbonate, and polycarbonate. Furthermore, the phenol product that contains acetol impurities tends to discolor upon aging, or during subsequent reactions, such as during sulfonation and chlorination reactions.

[0005] The acetol impurity has proven to be particularly difficult to remove from the phenol product in a downstream process since it co-distills at a similar temperature as phenol during thermal separation processes, e.g., rectification processes. Because of this, current thermal separation processes are generally ineffective at purifying the phenol product to remove the acetol impurity.

[0006] Various attempts have been made in the art to specifically reduce the amount of the acetol impurity from the phenol product. For example, various homogeneous and heterogeneous processes involving basic and acidic treating agents, such as treating the phenol product with sodium hydroxide, amines, ion-exchange resins, zeolites have been tried as well as two-step differential temperature treatments, and two-step chemical treatment processes. More specifically, a reaction product of an amine with an acidic material has been used to catalyze the cleavage, i.e., decomposition, of CHP isothermally in a controlled and selective manner in presence of excess acetone, excess cumene, and excess water. Another process for decomposing cumene hydroperoxide employs utilizing excess acetone of 10 to 100 % relative to the amount of acetone produced during the decomposition reaction in combination with up to 4 weight percent additional water relative to the water produced in the reaction mixture. These processes however aim at forming alpha-methyl styrene (AMS) as the byproduct, which is then hydrogenated to provide cumene. Depending upon the operating conditions employed, the acid-catalyzed cleavage of CHP for these different process generally produces from about 500 to about 2,500 parts per million (ppm) or more of acetol impurity. Moreover, the prior art processes tend to be cumbersome and involve numerous additional steps that increase the manufacturing costs for preparing the phenol and acetone products.

[0007] Therefore, a continuing need exists for a more effective method to reduce the level of acetol impurities in the phenol product that is produced by acid catalyzed cleavage of CHP, such as may be desired for producing higher quality aromatic bisphenols and polycarbonates therefrom. Such a process would desirably be a more economically favorable method for producing the purified phenol product.

#### BRIEF SUMMARY

[0008] A process for producing phenol, the process comprising introducing cumene hydroperoxide into a feedstream comprising phenol, acetone and an acid catalyst to produce a phenol product from the cumene hydroperoxide, wherein a molar ratio of the phenol to the acetone is greater than 1:1.

[0009] The present disclosure may be understood more readily by reference to the following detailed description of the various features of the disclosure and the examples included therein.

#### DETAILED DESCRIPTION

[0010] By implementing the process outlined in the present disclosure it is possible to improve the purity of the phenol product by suppressing the formation of acetol during the acid catalyzed cleavage process for phenol production. The process generally comprises cleaving CHP with the acid catalyst in the presence of an excess amount of phenol in the cleavage reactor, wherein the resulting phenol product has an acetol content of less than or equal to 400 ppm. As used herein, the term “excess amount of phenol” generally refers to a molar ratio of phenol to acetone that is greater than 1:1, i.e., greater than 1.

[0011] The use of the excess amount of phenol in the cleavage vessel(s) unexpectedly increases the overall efficiency, selectivity, and yield of the cleavage reaction. Moreover, a significant reduction of acetol impurity is observed during the acid catalyzed cleavage reaction. The molar ratio of phenol to acetone is preferably greater than 1:1, which is preferably maintained in the cleavage reactor during the acid catalyzed cleavage reaction. The molar ratio is periodically monitored to

maintain molar ratio of phenol to acetone greater than 1 in the feed stream and in the product stream by using gas chromatography techniques.

[0012] The process described hereinabove can be conducted either in a batch process, or in a semi-continuous process or a continuous process. In one embodiment, the feed stream is fed into a batch reactor where they are mixed by a motorized agitator, wherein, the feed stream comprises CHP, phenol, and acetone. The feed molar ratio of phenol to acetone is greater than 1:1, more specifically the feed molar ratio of phenol to acetone is greater than or equal to 1.5:1 and even more specifically the feed molar ratio of phenol to acetone is greater than or equal to 3:1. The phenol product is purified downstream of the batch reactor through a series of thermal separation units, or the like. Optionally, additional phenol is added to the feed stream comprising CHP to achieve a molar ratio of phenol to acetone greater than 1.

[0013] The concentration of CHP in the feed is generally maintained at 5 weight percent of the total amount of the feed, fed into the batch or continuous reactor. This helps to control the exothermicity of the reaction since higher concentration of CHP results in higher exotherm and potentially dangerous operating conditions. Cumene hydroperoxide used in the reaction is commercially available with a technical purity of 80 to 95 percent. Technical CHP used contains approx 82 wt% CHP, 7-15% Cumene, 2-5 wt% Dimethyl benzyl alcohol, 0.1-2 wt% Acetophenone.

[0014] The reaction being instantaneous, typically, the time taken for the decomposition in a batch mode is 30 seconds to 4 minutes and more specifically the time taken for the decomposition is 35 seconds to 3 minutes. However optimal conditions when coupled with other optimized parameters are from 45 seconds to 2 minutes in order to achieve a satisfactory decomposition of CHP and obtain a phenol product with an acetol content of less than or equal to 400 ppm.

[0015] The decomposition of cumene hydroperoxide is carried out at a temperature of 45°C to 75°C, more specifically the temperature is 50°C to 65°C, and even more specifically the temperature is 55°C to 60°C.

[0016] Any acid-catalyst can be used during the acid catalyzed decomposition of CHP, to provide the phenol and acetone products, in presence of excess phenol. The acid catalysts may be selected from the group consisting of mineral acids, strong organic acids, acidic clays, and acidic ion exchange resins. Exemplary acid-catalysts include, but are not intended to be limited to, sulphuric acid, phosphoric acid, p-toluene sulphonic acid, benzene sulphonic acid, trichloroacetic acid, acid-treated bentonite, a naturally occurring acidic clay and sulphonated styrene-divinyl benzene resin. In one embodiment, the acid-catalyst employed is sulphuric acid.

[0017] The quantity of catalyst used can vary substantially. The catalyst quantity employed is 50 parts per million (ppm) to 750 ppm of the feed composition, more specifically, 100 ppm to 650 ppm of the reactor composition, and even more specifically, 150 ppm to 600 ppm of the reactor composition.

[0018] The phenol product stream is then fed to a thermal separation unit, wherein the purified phenol can be separated and recovered. Thermal separation can be accomplished by using distillation techniques, or through other rectification methods.

[0019] In another embodiment, a process for enhancing the decomposition of CHP to phenol and acetone comprises adding water to the batch reactor during the acid catalyzed cleavage reaction. The amount of water is such that the total amount of water in the process does not exceed 5 weight % of the reactor composition.

[0020] The techniques described hereinabove enable the production of phenol with reduced acetol content in a single-step at relatively low operating temperatures. Advantageously, these techniques provide the ability to produce phenol and acetone at relatively high purity and with lower color, as well as the ability to operate the overall phenol production plant at a higher production rate, which represents a significant commercial advantage. Without being bound by theory, the higher production rate is a consequence of the lower levels of acetol present in the treated phenol stream produced as described above. A lower acetol level (i.e., an acetol concentration less

than 400 ppm) in the phenol product allows for a higher throughput in the downstream distillation operation, thereby leading to a lower cost process for producing purer phenol.

[0021] The phenol product obtained by the process may be used in the preparation of diphenylcarbonate or bisphenols. Diphenylcarbonate can be made by a variety of procedures including the phosgenation of phenol in an aqueous environment (slurry or melt) or in a solvent such as methylene chloride or by transesterification of dimethylcarbonate with phenol. A more direct procedure for making diphenylcarbonate involves the carbonylation of phenol with carbon monoxide. A transition metal catalyst such as a palladium catalyst is used in the carbonylation route often in combination with a quaternary ammonium halide as is generally known by those skilled in the art. Another procedure for making diphenylcarbonate involves the reaction between a cycloalkylene carbonate and phenol. Bisphenols may be synthesized by a condensation reaction between phenol and a carbonyl-containing compound in the presence of an acid catalyst. Numerous types of acid catalysts have been used in this type of condensation reaction including hydrochloric acid, perchloric acid, borontrifluoride as well as solid acid catalysts including zeolites, acid clays, heteropolyacids and ion-exchange resins.

[0022] The bisphenols and diphenyl carbonates can be used to prepare bisphenol polycarbonates by methods known in the art. Suitable methods of preparing the polycarbonates include, but are not intended to be limited to, an interfacial method, wherein bisphenol and phosgene or bisphenol and diphenyl carbonate are directly reacted in a molten state to undergo ester interchange reaction; an ester interchange that is usually effected at temperatures of 250°C or 330°C in presence of catalysts such as organic acid salts, inorganic acid salts, oxides, hydroxides or hydrides of metals or alcoholates; and a phase boundary process under catalysis by tertiary amines, tertiary amines may also be used for the preparation of polycarbonate through the reaction of bisphenol and phosgene. Alternately, a polycarbonate can be prepared by the reaction of diphenyl carbonate and bisphenol in presence of an alkaline catalyst at high temperatures by using a melt transesterification polymerization method.

[0023] A further understanding of the techniques described above can be obtained by reference to certain specific examples that are provided herein for purposes of illustration only, and are not intended to be limiting.

## EXAMPLES

[0024] HA Analysis was carried out on an Agilent 6890 Gas chromatograph (GC). GC separation was carried out on glass column length 24 inches & ¼ inch outer diameter, configured for on column injection, packed with chromsorb 102 80/100 mesh, with helium as carrier gas at 30ml/min. The injector temperature was 160 °C & detector temperature was 250 °C. The column is kept at an isothermal temperature of 160 °C. The run time was 25 minutes. The column was calibrated with standard HA (Aldrich, 97% pure) at a concentration ranging from 5 ppm to 244 ppm made in 50:50 cumene and phenol mixture.

[0025] Examples 1-3. In these examples, CHP was decomposed in a batch reactor to obtain a phenol product. The process generally included adding CHP feed (containing 82% CHP, 8 % dimethyl benzyl alcohol and rest cumene) to an agitated mixture of phenol, acetone and sulfuric acid. The amount of acetol was measured in the phenol product using gas chromatography techniques.

[0026] The process included the dropwise addition of cumene hydroperoxide in water (CHP, 82%, 1.0 mole) to a mixture of phenol, acetone, and sulfuric acid (300 ppm) at 45°C. The CHP addition was controlled to maintain a steady reflux temperature of 56°C. The results illustrating the effect of molar ratio on acetol production in the phenol product is shown in Table 1

[0027] Comparative Examples 1 and 2. In this example, CHP was decomposed in accordance with the procedure set forth in Examples 1-3, wherein the molar ratio of phenol to acetone content was less than 1:1. The moles of phenol and acetone included in Table 1 indicate the initial amount of phenol and acetone present in the reactor before the addition of CHP. The results are shown in Table 1.

Table 1.

Example	CHP, 82%	Phenol (moles)	Acetone (moles)	Molar Ratio	Acetol (ppm)
1	1.0	0.75	0.41	1.8 : 1	389
2	1.0	0.95	0.08	11.9 : 1	382
3	1.0	1.0	----	----	357
Comparative Example 1	1.0	0.5	0.81	0.62 : 1	446
Comparative Example 2	1.0	1.0	1.0	1:1	440

[0028] The data clearly shows that increasing the molar ratio of phenol to acetone decreases the amount of acetol formed during the acid catalyzed cleavage of CHP.

[0029] While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.